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Rapid, Low-Cost Analysis of a Copper Slag for 13 Elements by Flame Atomic Absorption Spectroscopy

By S. A. Matthes

UNITED STATES DEPARTMENT OF THE INTERIOR

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RAPID, LOW-COST ANALYSIS OF A COPPER SLAG FOR 13 ELEMENTS BY FLAME ATOMIC ABSORPTION SPECTROSCOPY

by

S. A. Matthes[1]

ABSTRACT

This Bureau of Mines report describes analysis of a copper slag for 13 elements from a single sample solution by flame atomic absorption spectroscopy. Samples are dissolved with 7 ml of an HCl-HF-HNO_3 (3:1.5:2) mixture in heated plastic pressure vessels. A 1.5-pct boric acid solution is added to dissolve precipitated fluorides and to reduce matrix effects that interfere with atomic absorption analysis. Preparation time is less than 1 hour per batch of 10 samples. Total analysis time is less than 6 person-hours for 130 determinations with an average relative standard deviation of 1.83 pct for the 13 elements. Simple acid standards were used for all determinations. Values obtained by this method are in excellent agreement with values obtained by slower, more costly procedures.

INTRODUCTION

A goal of the Bureau of Mines is the maintenance of an adequate supply of minerals and metals to meet the national economic and strategic needs. In support of this goal the Albany Research Center is conducting research related to the processing of copper ores. An integral part of the metallurgical studies is the determination of the major and minor constituents of copper reverberatory slags.

The analysis of copper slags presents the chemist with some unusual problems. A dozen or more elements may be present at levels above 0.1 pct, and the chemist may be asked to analyze each of them. Traditionally, a variety of methods of analysis have been required to determine the composition of each slag, because of the widely varying chemistry of the elements present. Arsenic and antimony are usually determined by distillation (3)[2] or by atomic absorption analysis of the hydride. Silicon is determined gravimetrically (3-4) after a lengthy dehydration procedure. Other elements are determined by a variety of spectrophotometric, titrametric, and gravimetric techniques or by

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[2]Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

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atomic absorption spectroscopy (AAS) after an acid digestion (8) in open platinum, glass, or Teflon[3] vessels; the vessel type is dependent on the acid mixture required for dissolution.

Recently, methods have been developed which allow the total analysis of a sample from a single solution by AAS. This laboratory previously reported such a method (2) involving an HCl-HNO_3-HF digestion in sealed plastic bottles, which act as pressure vessels when heated in a boiling-water bath. Boric acid is then added to create a fluoroboric acid matrix which prevents precipitation of insoluble fluorides and creates a relatively interference-free matrix for AAS analysis (1-2). This method has the following advantages: (1) Decomposition in a closed vessel prohibits volatile elements from escaping, (2) decomposition is carried out in a vessel resistant to acid attack that contains no contaminating elements, (3) decomposition under pressure requires a minimum amount of acid for very rapid dissolution, and (4) all elements are determined from a single solution. Using this method, a copper reverberatory slag was analyzed for 13 elements.

EXPERIMENTAL WORK

Equipment

1. Shatter box grinder.

2. Boiling and cold water baths.

3. Polycarbonate bottles, 250-ml, wide-mouthed with polypropylene screw caps. (See appendix.)

4. Teflon tape.

5. Bottle-holding rack (fig. 1). Fabricated from stainless steel or heat-resistant plastic. The plates are 30 cm in diameter, spaced 7.5 cm apart, and the bottle holes are 7.0 cm in diameter.

6. A 1- to 100-ml precision liquid dispenser.

7. Atomic absorption spectrophotometer with microprocessor, curve correction, and digital readout.

8. 50-mm nitrous oxide burner head.

9. Hollow cathode lamps for Mg, Ca, Al, Zn, Pb, Cu, Mn, Fe, Mo, Sb, Na, and Si and an Electrodeless Discharge Lamp (EDL) for As.

10. Welders'-grade acetylene, high-purity nitrous oxide, and dry and oil-free compressed air.

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[3]Reference to specific equipment does not imply endorsement by the Bureau of Mines.

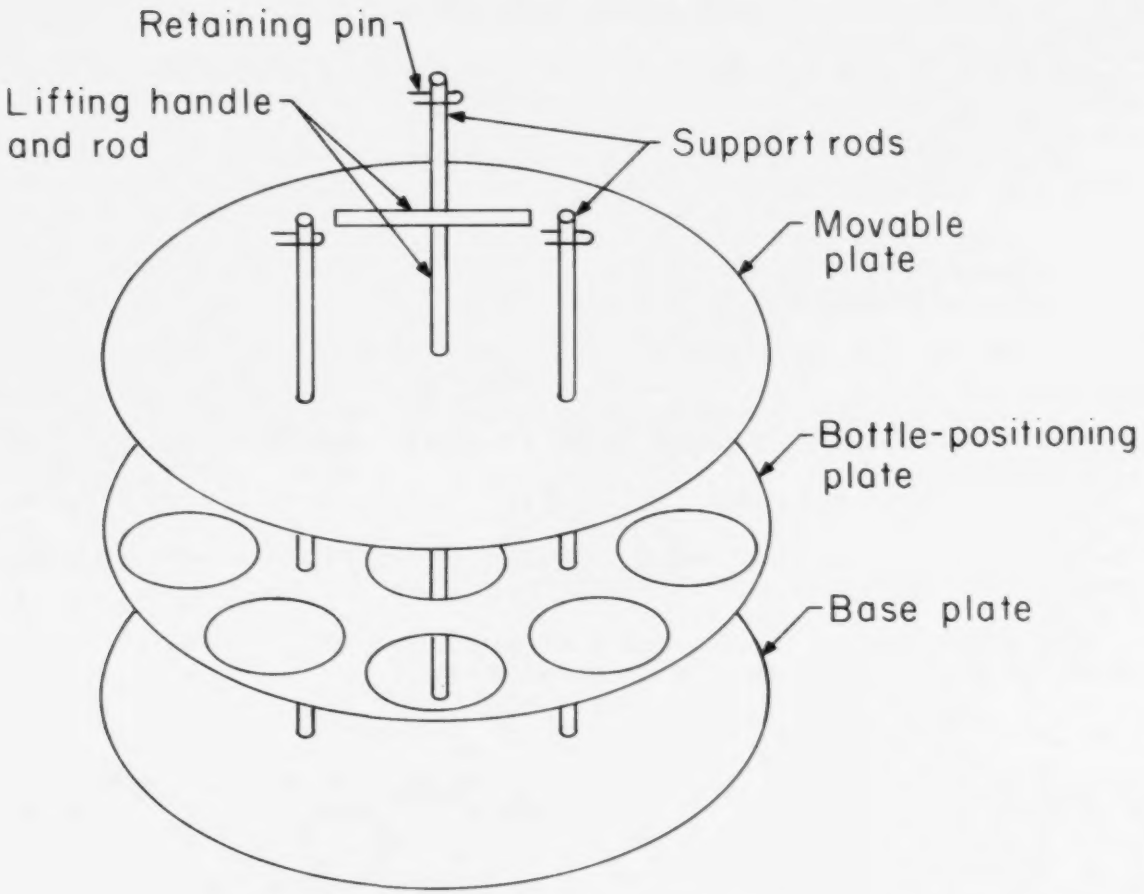

FIGURE 1. - Bottle-holding rack.

Reagents and Solutions

1. Boric acid solution (1.5 wt-pct) made by mixing 60 grams of high-purity boric acid crystals (99.99 pct) with 4,000 ml of H_2O.

2. a) HCl-HF acid mixture (7:3) made up with concentrated, reagent-grade acids.

b) HNO_3 - concentrated, reagent-grade acid.

3. Primary standard solutions of 1,000 μg/ml were prepared for each element from high-purity (99.9 pct) materials (7).

Sample Preparation

1. Grind all samples to pass 100 mesh.

2. Place 0.250-gram samples into 250-ml polycarbonate bottles.

3. Pipet (using a plastic pipet) a 5-ml 7:3 mixture of hydrochloric acid and hydrofluoric acid, followed by 2 ml of nitric acid, into each bottle.

4. Screw caps on tightly. Bottle threads are double-wrapped with Teflon tape.

5. Put bottles into bottle-holding rack and place the rack into the boiling-water bath for 15 minutes (fig. 2). The water level should be about 3 cm above the bottom of the plastic bottles.

6. Remove rack and bottles and cool in running water for 2 minutes.

7. When cool, remove caps from the bottles and add 93 ml of a 1.5 pct boric acid solution to each bottle, using a precision liquid dispenser.

8. Screw caps on tightly.

9. Put bottles into the bottle-holding rack and place the rack back into the boiling-water bath for 15 minutes.

10. Remove rack and bottles and place in cold water bath. When the final solutions are cool, they are ready for analysis.

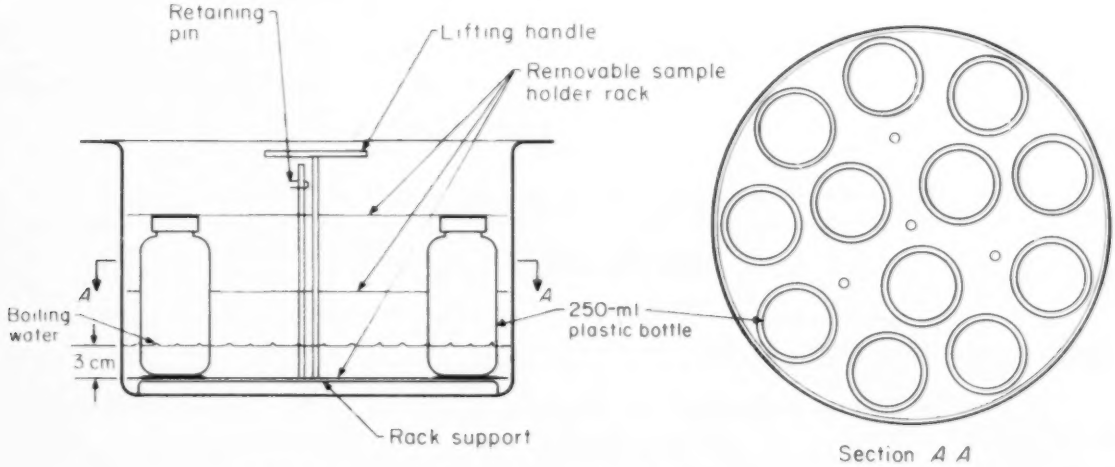

FIGURE 2. - Bottle-holding rack and boiling-water bath.

Analysis Procedure

After preparation, four dilutions of each sample solution are required to bring each element within standard range (table 1): (1) 10 to 1 with distilled H_2O, (2) 100 to 1 with distilled H_2O, (3) 50 to 1 with each dilution containing 0.8 g/l NaCl, (4) 2 to 1 with each dilution containing 4.0 g/l NaCl. All dilutions were made with singly distilled H_2O in class A volumetric glassware, using Eppendorf pipets.

TABLE 1. - Conditions for atomic absorption analysis of copper reverberatory slags

Element	Wave length, nm	Slit, nm	Lamp	Lamp current, Ma	Gas mix	Flame type	Dilution	Standards, µg/ml
Na.....	589.0	0.7	Na.....	12	Air-C_2H_3	Lean blue	10:1	1,2,5
Si.....	251.6	.2	Si.....	40	N_2O-C_2H_2	Rich red.	10:1	10,20,50
Mg.....	285.2	.7	Mg-Ca-Al	20	...do...	Lean blue	10:1	0.5,1,2
Ca.....	422.7	.2	...do...	20	...do...	Rich red.	50:1	1,2
Al.....	309.3	.2	...do...	20	...do...	...do....	2:1	10,20,50
As.....	193.7	.7	As (EDL)	[1]8	...do...	...do....	1	20,50
Mo.....	313.3	.7	Mo.....	30	...do...	...do....	1	5,10,20
Sb.....	217.6	.2	Sb.....	20	Air-C_2H_2	Lean blue	1	2,5,10
Mn.....	279.5	.2	Mn-Fe...	30	...do...	...do....	1	1,2,5
Fe.....	248.3	.2	...do...	30	N_2O-C_2H_2	...do....	100:1	2,5,10
Zn.....	213.9	.7	Zn-Pb-Cu	12	Air-C_2H_2	...do....	100:1	0.5,1,2
Pb.....	283.3	.7	...do...	12	...do...	...do....	1	5,10
Cu.....	324.7	.7	...do...	12	...do...	...do....	10:1	1,2,5

[1]Watts.

To minimize contamination and to maximize efficiency, elements were analyzed in a specific order using conditions listed in table 1. Simple dilutions of the primary standards were used for all elements. Calcium and aluminum contained 0.8 g/l and 4.0 g/l NaCl respectively in both samples and standards to correct for ionization effects in the flame (1-2).

A 50-mm titanium burner head was positioned at the optimum height for silicon analysis and was used at this height for analysis of all the other elements. Sodium and silicon were run first to reduce the risk of contamination by the leaching effect of the HF on the volumetric glassware. However, this order of analysis is not necessary since tests of solutions run 24 hours apart from the same flasks yielded identical results for the two elements. All of the elements requiring N_2O-C_2H_2 were run consecutively. Arsenic (6) was run next to last so that the arsenic EDL would have at least 1 hour to stabilize while the other elements were being analyzed.

RESULTS

The analytical data are summarized in table 2. The reported values listed at the bottom of table 2 were obtained by a variety of methods (3-5). SiO_2, CaO, and Al_2O_3 were obtained by gravimetric analysis, arsenic and

antimony by a distillation method, and iron by a titrimetric determination. Sodium, magnesium, molybdenum, and manganese were determined by AAS after dissolution in open platinum vessels. Zinc, lead, and copper were also determined by AAS following dissolution in open glass beakers. Results for AAS analysis of the bottle dissolution method were obtained from 10 different portions of the slag, which were put into solution as a batch. These results compare very closely to the reported values. In no case did the variation exceed 2.5 pct of the amount reported. The range of relative standard deviations is from 0.64 pct to 2.74 pct with an average of 1.83 pct.

TABLE 2. - Analytical data from analysis of copper reverberatory slag, percent

Bottle	Na	Si as SiO_2	Mg as MgO	Ca as CaO	Al as Al_2O_3	As	Mo	Sb	Mn	Fe	Zn	Pb	Cu
1.....	1.19	41.5	1.10	5.37	5.66	1.29	0.087	0.75	0.076	28.2	2.36	0.93	0.43
2.....	1.26	41.1	1.11	5.16	5.83	1.36	.093	.77	.077	28.1	2.45	.98	.45
3.....	1.26	41.6	1.11	5.16	5.69	1.36	.092	.78	.077	28.3	2.45	.98	.45
4.....	1.24	41.1	1.11	5.19	5.78	1.38	.092	.78	.077	28.4	2.41	.97	.45
5.....	1.24	41.8	1.11	5.34	5.82	1.39	.093	.78	.077	28.2	2.41	.97	.45
6.....	1.23	41.9	1.13	5.11	5.84	1.33	.091	.76	.076	28.3	2.39	.96	.44
7.....	1.22	41.3	1.11	5.16	5.47	1.34	.091	.79	.077	28.4	2.38	.96	.44
8.....	1.22	41.3	1.11	5.14	5.60	1.34	.091	.76	.075	28.2	2.40	.95	.44
9.....	1.19	41.5	1.13	5.14	5.52	1.33	.089	.75	.074	28.1	2.32	.94	.44
10.....	1.26	41.5	1.11	5.24	5.59	1.40	.095	.82	.078	28.8	2.49	.99	.46
Average.	1.23	41.5	1.11	5.20	5.68	1.35	.097	.77	.077	28.3	2.44	.96	.45
RSD[1]....	2.15	.64	.85	1.70	2.37	2.44	2.43	2.74	1.87	.73	2.03	1.96	1.89
Reported values.	1.22	42.4	1.12	5.10	5.73	1.36	.098	.77	.076	28.8	2.45	.96	.45

[1]Relative standard deviation.

DISCUSSION AND CONCLUSION

Using the conditions listed in table 1, no analytical interferences were encountered. An apparent interference of the boric acid matrix on the determination of aluminum reported previously (1-2) was eliminated by reducing the slit from 0.7 nm to 0.2 nm. A similar depression in the absorbance of iron was eliminated by running iron determinations with the N_2O-C_2H_2 flame (2).

The method presented in this paper offers an effective way of determining the major and minor constituents of copper slags. Because of the small amount of acid required, the rapid analysis time, and its good precision, this method is superior to other methods currently used for the analysis of slags. The ability to dissolve and to keep in one solution a wide variety of elements without loss makes this procedure an excellent analytical technique for the determination of most inorganic materials.

REFERENCES

1. Farrell, R. F., A. J. Mackie, and W. R. Lessick. Analysis of Steelmaking Slags by Atomic Absorption Spectrophotometry Using Pressure Dissolution. BuMines RI 8336, 1979, 11 pp.

2. Farrell, R. F., S. A. Matthes, and A. J. Mackie. A Simple Low-Cost Method for the Dissolution of Metal and Mineral Samples in Plastic Pressure Vessels. BuMines RI 8480, 1980.

3. Furman, N. H. (ed.). Scott's Methods of Chemical Analysis. D. Van Nostrand Co., Inc., New York, v. 1, 5th ed., 1947, 1234 pp.

4. _____. Scott's Methods of Chemical Analysis. D. Van Nostrand Co., Inc., New York, v. 2, 5th ed., 1947, pp. 2020-2021.

5. Hildebrand, W. F., and G. E. F. Lendell. Applied Inorganic Analysis. John Wiley & Sons, Inc., New York, 1953, 1034 pp.

6. Likaits, E. R., R. F. Farrell, and A. J. Mackie. Determination of Arsenic in Blister Copper and Flue Dust by Atomic Absorption Spectroscopy. Atomic Absorption Newsletter, v. 18, No. 2, 1979, pp. 53-54.

7. Smith, B. W., and M. L. Parsons. Preparation of Standard Solutions. Critically Selected Compounds. J. Chem. Educ., v. 50, No. 10, 1973, pp. 679-681.

8. Sulcek, Z., and P. Povondra. Decomposition Procedures in Inorganic Analysis. CRC Critical Reviews in Analytical Chemistry, v. 6, No. 3, 1977, pp. 266-280.

APPENDIX.--POLYCARBONATE BOTTLES

Polycarbonate is an inexpensive, high-tensile-strength, heat-resistant, and acid-resistant plastic; it is transparent, rigid, unbreakable, nontoxic, and the toughest of the thermoplastics. The bottles used by this laboratory are Autoclear polycarbonate bottles, IEC No. 2051, Polycarbonate bottles, Nalge No. 3122-0250, and Nalgene Sample Digestion Vessels.

A boiling-water bath with at least 15-cm-high sidewalls is recommended to contain any possible acid leaks from the bottles, although the internal pressure in the bottles is not sufficient to create a safety hazard. The bottle-holding rack is designed to prevent the bottles from floating in the water bath. The apparatus is shown in main-text figures 1 and 2.

During the dissolution process some acid fumes may leak around the caps of the bottles. Although this leakage should not affect the analytical results, it creates a health hazard, requiring the procedure to be carried out in a fume hood.

Using the recommended equipment and acid mixture, bottle lifetime should be about 10 runs. A gradual yellowing and increasing opaqueness of the plastic is normal with bottle use.

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